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(54) Method of preparation of porous carbon material and material produced by the method.

(57) A porous carbon material is prepared by (a) forming a carbonizable polymer structure having a porous structure of cells and optionally pores interconnecting the cells by condensation polymerization in which polymerization precursors are present in the continuous phase of a high internal phase oil-in-water emulsion and (b) carbonizing the carbonizable polymer structure by heating in an inert atmosphere to at least 500°C. The internal (oil) phase of the emulsion may be at least 74% by volume. The material produced has high strength.

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METHOD OF PREPARATION OF POROUS CARBON MATERIAL AND MATERIAL PRODUCED BY THE METHOD

This invention relates to a method of preparation of porous carbon material and material produced by the method. The material may be in the form of a monolithic body, e.g. block or sheet, or in granular form.

It is known to form porous carbon material by carbonization of foamed organic compositions. Most disclosures relate to polyurethanes (e.g. US-A-4 124 691). US-A-3 859 421 describes carbonization of a dispersed carbon-yielding organic binder in a continuous liquid pore-forming phase. It is known to carbonize phenol/formaldehyde resins. US-A-3 342 555 and CA-A-733558 disclose carbonization of a foamed phenol/formaldehyde resin to give a product with relatively large pore size (0.1 - 0.4 mm). GB-A-2 035 282 describes carbonization of a phenol/formaldehyde resin which is absorbed in the pores of silica particles which act as a template; after carbonization the silica is removed with acid to give a porous particulate product. EP-A-196 055 describes removal of an inorganic salt from a cured phenol/formaldehyde resin, to form pores. The porous structure is then carbonized.

EP-A-223574 describes a porous carbon structure consisting of concave surfaces and having at least 80% voids and comprising cavities joined by interconnecting pores, with a density of less than 0.5 g/cm^3. This structure is made by carbonization, achieved by heating up, to for example 1000 °C with careful control of heating rate, certain porous vinyl-type polymeric materials. These materials are made by polymerization of a high internal phase emulsion comprising as a non-aqueous continuous phase a monomer and cross-linking agent and as the discontinuous or internal phase water or an aqueous solution.

It has now been found that porous carbon materials, which are similar to those of EP-A-223574 but improved in some respects, can be made by carbonization of porous polymeric structures formed in a different manner, in particular by condensation polymerization of the continuous phase of a high internal phase emulsion. The continuous phase is aqueous and the internal phase is non-aqueous. It is therefore an object of the invention to provide an improved porous carbon material and an improved method of preparing it.

According to the present invention there is provided a method of preparing a porous carbon material, comprising (a) forming a carbonizable polymer structure having a porous structure of cells and optionally pores interconnecting the cells by condensation polymerization in which polymerization precursors are present in the continuous phase of a high internal phase oil-in-water emulsion and (b) carbonizing the carbonizable polymer structure by heating in an inert atmosphere to at least 500 °C. The internal (oil) phase of the emulsion is preferably at least 74% by volume. The carbonized product may have a void volume as high as 90-96%.

The porous carbon material of the invention has, like that of EP-A-223574, generally concave surfaces, with generally spherical cells. The cell size is preferably in the range 1-100 µm. The pores or holes interconnecting the cells may have a mean size of 0 µm (representing closed cells) to 80 µm, preferably 0.1-50 µm, more preferably 0.5-10 µm. The carbonizable polymer structure having closed cells requires slow drying to remove the internal phase before carbonization.

By the invention, it is possible to achieve a narrow range of size of the interconnecting pores in a carbonized body. Preferably this size range is substantially in the range 40% to 250% of the mean pore size, more preferably 50% to 200%.

Generally, the heating step for carbonization can be as described in EP-A-223574. In the present invention, the temperature rise rate is preferably not more than 2 °C per minute between 300 °C and 500 °C, more preferably between 200 °C and 700 °C. Preferably the carbonization is conducted so that the bulk volume shrinkage of the polymer structure is in the range 40-60%, and preferably also the void fraction (i.e. the void volume expressed as a percentage of the bulk volume) remains substantially unchanged. The porous carbon structure may be produced substantially free of microcracks.

The porous carbon structure of the invention may be a monolithic body, such as a block or sheet, made from a carbonizable polymer structure in the form of a block or sheet. Alternatively, the carbonizable product of the polymerization step may be granulated before carbonization, to produce a particulate porous carbon material.

Methods of making the porous carbonizable polymer structure by condensation polymerization are fully described in EP-A-289238, the contents of which are herein incorporated by reference. In the present invention, it is preferred to use a cross-linked polymer for carbonization. Generally preferred in the present invention are condensation polymerization systems based on phenols and aldehydes, e.g. phenol/formaldehyde, resorcinol/formaldehyde and orcinol/formaldehyde. Polyvinyl alcohol may be included in the phenol-formaldehyde system. Alternative useful systems are urea-formaldehyde, melamine-formal-

dehyde and systems based on the condensation of an amino group and an acid group. Pre-polymerization may be necessary before formation of the emulsion.

The internal phase in the emulsion is non-polar and is desirably a material which evaporates on heating and is not degraded to form a residue. Alkanes, e.g. cyclohexane, heptane, paraffins, in particular are preferred since they do not need drying out of the polymerization product, but evaporate on heating for carbonization. This is an advantage over the process of EP-A-223574 which uses vinyl-type porous polymers which must be washed before carbonization.

One advantage obtainable with the method of the present invention, compared with that of EP-A-223574 can be better retention of shape of the carbonizable polymer structure during carbonization. Shrinkage occurs uniformly during carbonization, and distortion of the structure can be avoided. Another advantage can be higher yield. A third advantage can be higher compressive strength at the same void volume in the carbonized product, perhaps due to an absence of, or fewer, microcracks.

The structure and appearance of the porous carbon material produced in the present invention are similar to those of the materials of EP-A-223574 and reference should be made to that specification for an illustration.

The porous carbon material producred by the present invention has many uses, e.g. as adsorbent, and in catalysis, filtration and chromatography.

The invention will now be illustrated by examples and one comparative example.

The following standard procedure was used:-

High internal phase emulsions were formed as follows. An aqueous solution of condensation polymer precursor was mixed with a surfactant. To the mixture, while stirring, was slowly added an immiscible oil internal phase up to the appropriate phase volume. The stirrer used was a Teflon blade 6 cm diameter and about 1 cm high at its mid-point rotated about a vertical axis. The resulting emulsion was stirred as required to form internal phase droplets of the desired size distribution. An acid polymerization catalyst was then added and then thoroughly stirred in. The resulting castable fluid was cured at an appropriate temperature into a porous monolithic body and dried.

The dry condensation polymer bodies were then subject to controlled pyrolysis in an oxygen-free nitrogen purged atmosphere using a T105/6 furnace of Severn Scientific Ltd. and a 1000 mm x 80 diameter mullite work tube in conjunction with a Eurotherm 820 programmer-controller.

Traces of water were removed from the inlet gas by passing it over a molecular sieve and phosphorus pentoxide prior to passing through the work tube. A gas flow rate of typically 100 cm^3 in^{-1} was maintained throughout the temperature program. The heating rate was limited to minimised stress-cracking of the polymer during carbonization.

Details are given in each Example below.

Two temperature profiles were used in the carbonization step:-

Profile 1

from 25°C to 160°C 2°C per minute
from 160°C to 700°C 1°C per minute
from 700°C to 1000°C 2°C per minute
at 1000°C dwell for 60 minutes
from 1000°C to 25°C 1°C per minute

Profile 2

from 25°C to 160°C 2°C per minute
from 160°C to 600°C 1°C per minute
from 600°C to 1100°C 2°C per minute
at 1100°C dwell for 120 minutes
from 1100°C to 25°C 2°C per minute.

All of the carbonizable porous polymer structures of this invention were salmon-pink on polymerization, changing to rust brown over several days.

Example 1

Continuous phase

phenol-formaldehyde resin* - 15 g
water - 8 g
*phenol-formaldehyde pre-polymer formed as described in "Experimental Plastics" (C A Redfern and J Bedford, 2nd Edition, 1980, Iliffe & Sons Ltd. page 7)

Internal phase

light liquid paraffin - 50 ml

Emulsion, internal phase volume

- 82%

Polymerization catalyst

toluene-4 sulphonic acid (70% w/v) - 6 g

Mixing

Surfactant

5 mins, 500 rpm
Mirinol + C2M-SF conc - 25 g
+ Mirinol is an amphoteric surfactant of Venture Chemical Products Ltd., Tilehurst, Reading, UK

Curing

12 hours, 60 °C

Carbonization profile

1

Example 2

Continuous phase

phenol-formaldehyde resin* - 15 g
water - 8 g
* as in Example 1

Internal phase

light paraffin - 170 ml

Emulsion, internal phase volume

- 92%

Polymerization catalyst

toluene-4 sulphonic acid (70% w/v)
- 6 g

Mixing

5 mins, 500 rpm

Surfactant

Mirinol C2M-SF conc - 25 g

Curing

12 hours, 60° C

Carbonization profile

1

Example 3

Continuous phase

phenol-formaldehyde resin* - 15 g
polyvinyl alcohol (mol.wt. 72000) - 1.2 g
aqueous 40% w/v formaldehyde - 3 ml
* as in Example 1

Internal phase

light paraffin - 110 ml

Emulsion, internal phase volume

- 94%

Polymerization catalyst

toluene-4 sulphonic acid (70% w/v)
- 6 g

Mixing

5 mins, 500 rpm

Surfactant

Mirinol C2M-SF conc - 25 g

Curing

12 hours, 60° C

Carbonization profile

1

Example 4

Continuous phase

phenol-formaldehyde resin* - 15 g
aqueous 40% w/v formaldehyde - 8 g
* as in Example 1

Internal phase

light paraffin - 170 ml

Emulsion, internal phase volume

- 93%

Polymerization catalyst

toluene-4 sulphonic acid (70% w/v)
- 6 g

Mixing

5 mins, 500 rpm

Surfactant

Mirinol C2M-SF conc - 25 g

Curing

12 hours, 60°C

Carbonization profile

1

Example 5

Continuous phase

resorcinol - 16.6 g
aqueous 40% w/v formaldehyde - 24.4 g

Internal phase

cyclohexane - 360 ml

Emulsion, internal phase volume

- 90 %

Polymerization catalyst

conc HCl - 1.7 ml water - 20 ml

Mixing

1 min, 800 rpm

Surfactant

Mirinol C2M-SF conc - 4.54 g

Curing

10 mins, 25° C

Carbonization profile

2

Example 6

Continuous phase

resorcinol - 16.6 g
aqueous 40% w/v formaldehyde - 24.4 g

Internal phase

n-heptane - 360 ml

Emulsion, internal phase volume

- 90 %

Polymerization catalyst

conc HCl - 1.9 ml water - 20 ml

Mixing

2 min, 500 rpm

Surfactant

Mirinol C2M-SF conc - 4.54 g

Curing

5 mins, 25° C

Carbonization profile

1

Example 7

Continuous phase

resorcinol - 16.6 g
aqueous 40% w/v formaldehyde - 24.4 g

Internal phase

n-heptane - 360 ml

Emulsion, internal phase volume

- 90 %

Polymerization catalyst

conc HCl - 1.9 ml
water - 20 ml

Mixing

2 mins, 500 rpm
10 mins, 800 rpm

Surfactant

Mirinol C2M-SF conc - 4.54 g

Curing

5 mins, 25° C

Carbonization profile

1

Chemical analysis of carbonizable polymer and carbon product:

carbonizable polymer C 60.15% H 4.96%
carbonized product C 96.80% H 0.62%

Example 8

Continuous phase

resorcinol - 24.9 g
aqueous 40% w/v formaldehyde - 36.6 g

Internal phase

n-heptane - 204 ml

Emulsion, internal phase volume

- 80 %

Polymerization catalyst

conc HCl - 3.8 ml
water - 20 ml

Mixing

2 mins, 500 rpm

Surfactant

Mirinol C2M-SF conc - 6.82 g

Curing

5 mins, 25° C

Carbonization profile

1

Example 9

Continuous phase

resorcinol - 24.9 g
aqueous 40% w/v formaldehyde - 36.6 g

Internal phase

n-heptane - 204 ml

Emulsion, internal phase volume

- 80 %

Polymerization catalyst

conc HCl - 3.8 ml
water - 20 ml

Mixing

2 mins, 500 rpm
10 mins, 800 rpm

Surfactant

Mirinol C2M-SF conc - 6.82 g

Curing

5 mins, 25° C

Carbonization profile

1

Various calculations and measurements of structure and strength were made in respect of the intermediate carbonizable polymer and the final porous carbon product of each of Examples 6 to 9 and of the Comparative Example A. The results are set out in Table 1. The products of the Examples of the invention and of Comparative Example A consist of a carbonized monolithic matrix having a porosity formed by cells interconnected by pores.

The Comparative Example A is a porous carbon body formed from a vinyl polymer according to the process of EP 223574, using as the continuous phase of the emulsion methacrylonitrile 7cc, divinylbenzene (55% solution in ethylvinylbenzene) 4cc, surfactant Span 80 (ICI) 2g, and as the internal phase 100cc aqueous solution of initiator (potassium persulphate 2.5 g/l (0.013 molar) and $CaCl_2$ 0.1 molar).

The results show considerably higher strength achieved with the process of the present invention. Note that the carbonized body of the Comparative Example has a smaller cell size and therefore may be expected to be stronger than the bodies of Examples 8 and 9 of the same void volume. In fact it is weaker.

The four Figures accompanying this specification are SEMs (Scanning Electron Micrographs) obtained in conventional manner. The magnification is given by the scale bar. Fig. 1 shows the carbonizable polymer of Example 8 and Fig. 2 shows the carbon body produced in Example 8. Likewise, Figs. 3 and 4 are respectively the carbonizable polymer and the carbon body of Example 9.

TABLE 1

Example	6	7	8	9	A
Carbonizable polymer					
density $g.cm^{-3}$	0.079	0.084	0.14	0.14	0.068
void volume (%)$^{+}$	94	93	89	89	90
compressive modulus ($Nm^2 \times 10^{-6}$)	6.8	5.1	10	17	4.8
compressive strength ($Nm^2 \times 10^{-6}$)	0.74	0.8	1.7	2.0	0.6
mean cell size (μm)$^{++}$	50	10	25	5	2
mean pore size (μm)$^{+++}$	5	.1.3	5	0.8	-
Carbon body					
density $g.cm^{-3}$	0.092	0.086	0.14	0.14	0.10
void volume (%)$^{+}$	94	94	90	90	90
compressive modulus ($Nm^2 \times 10^{-6}$)	10	15	20	30	18
compressive strength ($Nm^2 \times 10^{-6}$)	1.5	2.0	3.5	5.2	2.3
mean cell size (μm)$^{++}$	40	10	15	5	2
mean pore size (μm)$^{+++}$	5	1.0	4	0.6	-
pore size range (μm)$^{+++}$	2-12	0.5-2	2-6	0.3-1.1	-

Notes for Table 1

+ calculated assuming density of solid resorcinol-formaldehyde polymer is 1.26 $g.cm^{-3}$, density of polymethacrylonitrile is 1.1 $g.cm^{-3}$ and density of amorphous carbon is 1.45 $g.cm^{-3}$

+ + estimated from scanning electron microscope pictures

+ + + obtained by mercury intrusion porosimetry

All the carbonizable polymers in the Examples of the invention had electrical resistivities greater than 10^{12} Ω.m. All the carbonized materials had electrical resistivities of less than 1 Ω.m. All the carbonized bodies in the Examples are substantially crack free.

Claims

1. A method of preparing a porous carbon material, comprising (a) forming a carbonizable polymer structure having a porous structure of cells and optionally pores interconnecting the cells by condensation polymerization in which polymerization precursors are present in the continuous phase of a high internal phase oil-in-water emulsion and (b) carbonizing the carbonizable polymer structure by heating in an inert atmosphere to at least 500 °C.

2. A method according to claim 1 wherein the internal (oil) phase of the emulsion is at least 74% by volume.

3. A method according to claim 1 or claim 2 wherein the average cell size of the porous carbon material produced is in the range 1 - 100 µm.

4. A method according to any one of claims 1 to 3 wherein the porous carbon material produced has pores interconnecting said cells, of an average size less than the average cell size and in the range 0.1 to 50 µm.

5. A method according to any one of claims 1 to 4 wherein in step (b), the carbonizable polymer is heated up at a temperature rise rate of not more than 2° C per minute between 300 and 500° C.

6. A method according to claim 5 wherein the heating in step (b) is conducted to at least 700° C and the temperature rise rate between 200 and 700° C is not more than 2° C per minute.

7. A method according to any one of claims 1 to 6 wherein the polymerization precursors are a condensation polymerization system selected from the group comprising
a phenol-aldehyde system,
a urea-formaldehyde system,
a melamine-formaldehyde system, and
a system based on condensation of an organic amino group and an organic acid group.

8. A method according to any one of the preceding claims wherein the internal phase in the emulsion is a material which evaporates on heating without forming a residue.

9. A method according to claim 8 wherein the internal phase in the emulsion is an alkane or mixture of alkanes.

10. A porous carbon material produced by the method of any one of the preceding claims.

Fig.1.

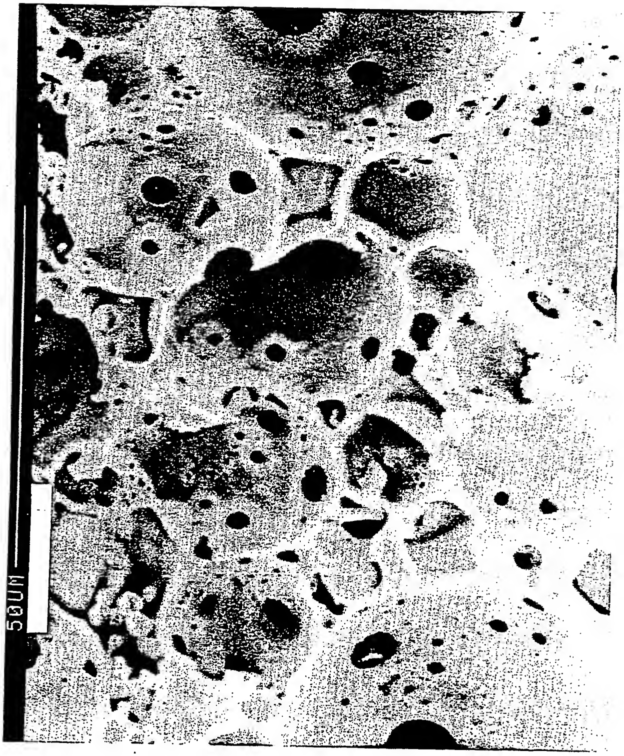


Fig.2.

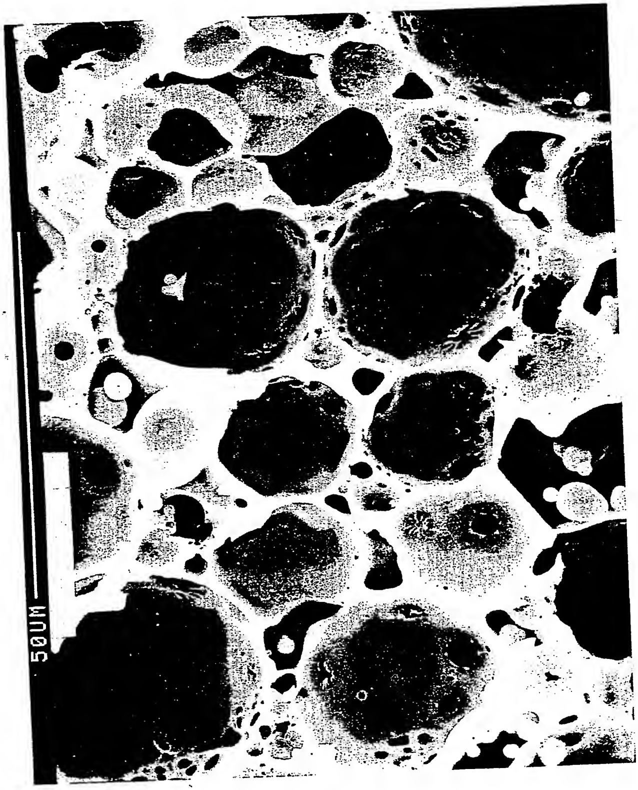


Fig.3.

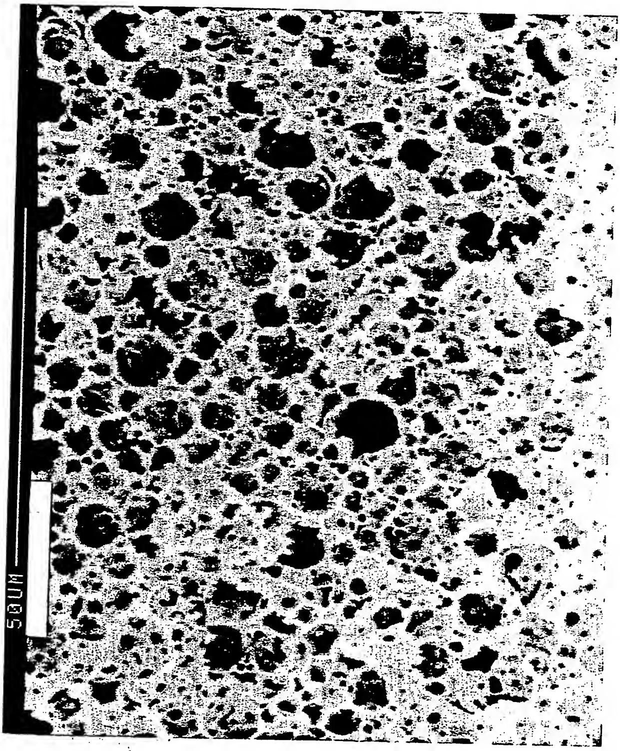
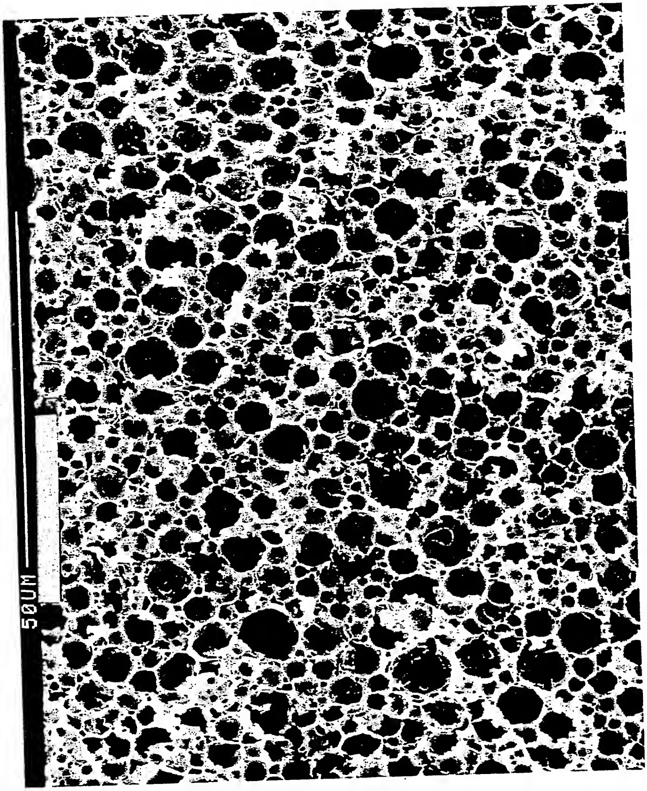


Fig.4.



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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 0766

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	US-A-3342555 (W.J.MCMILLAN) * claims *	1, 5-7, 10	C04B38/00
D,Y	EP-A-223574 (UNILEVER PLC) * page 2, line 16 - page 2, line 58 *	1, 5-7, 10	
A	US-A-4022875 (VINTON ET AL) * claims *	1	
A	CHEMICAL ABSTRACTS, vol. 75, no. 24, 13 December 1971 Columbus, Ohio, USA page 27; ref. no. 14156U & JP-A-7121446 (TOYO RUBBER INDUSTRY) 17-06-1971 * abstract *	1, 8	
D,A	FR-A-2385762 (CHEMOTRONICS INTERNATIONAL INC) * page 7, line 24 - page 8, line 14; claims 1, 5-8 *	1, 5, 6	
A	EP-A-200528 (UNILEVER PLC) * claims 1-3, 5, 6 *	1-4, 8	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)** C04B C08J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 JULY 1990	THEODORIDOU E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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